

"PROCESS FOR PRODUCING POLYMERS OF ETHYLENICALLY UNSATURATED
MONOMERS AND A COMPOSITION FOR USE AS CATALYST IN SAID
PROCESS"

5 The present invention relates to a process for producing
polymers (both homopolymers and copolymers) of ethylenically
unsaturated compounds, especially olefins, (hereinafter, for
convenience, referred to as "olefin polymers") and to a composition
which may be used as a component of a highly active catalyst
in such a process.

10 It is well known to use the so-called "Ziegler" catalysts
for the polymerization of olefins. Such catalysts comprise
a transition metal compound of a metal from Group IVb to Group
VIb and an organometallic compound of a metal from Group I
to Group III of the Periodic Table of the Elements. Subsequently,
15 many studies have been carried out to investigate the behaviour
of supported catalysts, comprising a transition metal compound
supported on various types of carrier. Carriers which have
been found to be effective include such inorganic compounds
as oxides, hydroxides, chlorides and carbonates of metals and
20 of silicon, mixtures of these compounds and double salts.
Of these inorganic compounds, particularly effective compounds
are magnesium compounds, such as the magnesium halides, as
described in Japanese Patent Publications No. 12105/64 and
No. 41676/72. Also highly effective are alkoxymagnesium and
25 aryloxymagnesium compounds, as described in Japanese Patent
Publications No. 34098/71 and No. 42137/72 and in Japanese
Patent Applications Kokai (i.e. as laid open to public inspection)

No. 119982/74, No. 147688/77, No. 133408/80 and No. 144006/80. Known catalyst systems using these carriers have a relatively high, albeit not sufficiently high, activity and, in addition, the polymers which are formed are unsatisfactory with regard to their degree of stereoregularity, particularly polymers of α -olefins having 3 or more carbon atoms. Moreover, these catalyst systems generally give polymers having a broad particle size distribution and do not produce polymers having a controlled particle size with a narrow distribution. Although there have been many attempts to improve the catalysts in these respects, as yet the improvements obtained have not been wholly satisfactory.

Furthermore, when producing olefin polymers, it is desirable that the polymers should contain the least possible amount of catalyst residues, since the inclusion of these residues in the polymer can give rise to various problems associated with the stability and processability of the polymer. As a result, it is generally necessary to provide a post-treatment unit in order to remove these catalyst residues and to stabilize the olefin polymers; provision of such a unit, of course, adds to the expense of producing the polymer. This disadvantage can be overcome if it is possible to increase the activity of the catalyst (expressed in terms of the weight of polymer formed per unit weight of the catalyst). If the catalyst activity is sufficiently high that relatively small quantities of catalyst can be employed and, as a result, the quantity of catalyst residues left in the polymer is relatively small, then it is

no longer necessary to provide any installation for removing catalyst residues and the production cost of the polymer can be reduced; this is the so-called "non-deashing process".

On the other hand, when an olefin is polymerized by
5 the slurry method or the gas phase method, the bulk density, average particle size and particle size distribution of the resulting polymer are important factors which affect the productivity. Improving these factors will result in a reduction in the adhesion of polymer to the walls of the polymerization
10 vessel, an improvement in the efficiency of utilization of the reactor and an improvement in the efficiencies of transporting, drying and granulating the polymer; these improvements can lead to an increase in productivity and a reduction in polymer cost. Provided sufficient improvement is achieved, it may
15 even be possible to employ powder moulding, which eliminates the granulation step. However, olefin polymers formed using a supported catalyst generally have the disadvantages of low bulk density, small average particle size and a broad particle size distribution. Accordingly, it is of considerable commercial
20 importance to develop a supported catalyst which can be used in the non-deashing process and which is capable of producing an olefin polymer having a high bulk density and a narrow particle size distribution.

Japanese Patent Application Kokai No. 133408/80 discloses that a highly active catalyst for the preparation of highly stereoregular olefin polymers can be obtained by supporting a titanium compound on the carrier formed by reacting a solid organomagnesium halide, a phenol and an aromatic carboxylate ester. We have now discovered a solid carrier useful in preparing a supported catalyst which has a high activity (expressed as the amount of polymer either per unit weight of the transition metal or per unit weight of the solid catalyst component), which means that the catalyst may be used in the non-deashing process and, moreover, the polymer produced with this catalyst has a narrow particle size distribution and forms a slurry having desirable properties.

The present invention accordingly consists in a solid composition comprising a titanium compound and/or a vanadium compound supported on a solid product formed from the reaction of (i) a phenol, (ii) an aromatic carboxylate ester and (iii) a solid reaction product of an organomagnesium compound and an aryloxyaluminium compound of general formula $Al(OR^1)_3$, (in which R^1 represents an aryl group having from 6 to 20 carbon atoms).

The invention further consists in a process for preparing a polymer by polymerizing an ethylenically unsaturated compound,

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especially a hydrocarbon, e.g. an olefin in the presence of a catalyst system comprising:

(a) a solid composition according to the invention; and

(b) an organoaluminium compound.

5 The organomagnesium compound used in the synthesis of the reaction product (iii) is preferably such a compound which is prepared by or is capable of being prepared by the reaction of an organic halogen compound with metallic magnesium. Especially suitable are Grignard compounds, which may be represented by
10 the general formula R^2MgX (in which R^2 represents a hydrocarbon group having from 1 to 20 carbon atoms and X represents a halogen atom), and dihydrocarbylmagnesium compounds, which may be represented by the general formula R^2_2Mg (in which R^2 is as defined above). In the above formulae, the hydrocarbon group represented by
15 R^2 may be an alkyl, aryl, aralkyl or alkenyl group having from 1 to 20 carbon atoms, for example a methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, t-butyl, pentyl, isopentyl, hexyl, octyl, 2-ethylhexyl, phenyl or benzyl group. X preferably represents a chlorine, bromine or iodine atom.

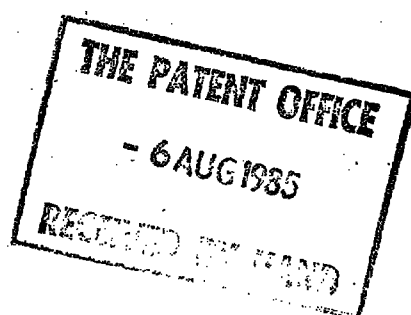
20 Specific examples of such Grignard compounds include ethylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium iodide, propylmagnesium chloride, propylmagnesium bromide, butylmagnesium chloride, butylmagnesium bromide, pentylmagnesium

chloride, phenylmagnesium chloride and phenylmagnesium bromide. Specific examples of dihydrocarbylmagnesium compounds include diethylmagnesium, dipropylmagnesium, dibutylmagnesium, dipentylmagnesium and diphenylmagnesium.

5 The synthesis of such organomagnesium compounds is preferably carried out in the presence of a solvent, most especially an ether, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, dipentyl ether, diisopentyl ether, dihexyl ether, dioctyl ether, diphenyl ether, dibenzyl
10 ether, phenetole, anisole, tetrahydrofuran or tetrahydropyran. It is also possible to use hydrocarbons (such as hexane, heptane, octane, cyclohexane, methylcyclohexane, benzene, toluene or xylene) and mixtures of ether and hydrocarbon solvents. In
d the synthesis of the solid carrier, the organomagnesium compound
15 is preferably used in the form of a solution in an ether or as an ether complex. We most prefer to use a Grignard compound of formula R^2MgCl (in which R^2 is as defined above) in the form of an ether solution or ether complex.

20 Examples of aryloxyaluminium compounds, which may be represented by the general formula $Al(OR^1)_3$ (in which R^1 represents an aryl group having from 6 to 20 carbon atoms), which are the other reagent employed to produce the reaction product (iii), include aluminium triphenoxide, aluminium tri-o-cresoxide, aluminium tri-m-cresoxide, aluminium tri-p-cresoxide, aluminium
25 tri-2,6-dimethylphenoxide, aluminium tri-2,3-dimethylphenoxide,

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aluminium tri-2,4-dimethylphenoxide, aluminium tri-3,5-dimethylphenoxide, aluminium tri-o-ethylphenoxide, aluminium tri-m-ethylphenoxide, aluminium tri-p-ethylphenoxide, aluminium tri-2,6-di-t-butylphenoxide, di-o-cresoxyaluminium phenoxide, diphenoxy-
5 aluminium o-cresoxide and aluminium trinaphthoxide. These compounds may be synthesized by known methods, for example by reacting a trialkylaluminium with a phenol or by reacting aluminium trimethoxide with a phenol.

~~The~~ The phenol (i), which is used to prepare the solid carrier
10 employed in the composition of the invention, is preferably a monohydric phenol, for example phenol, o-cresol, m-cresol, p-cresol, 2,6-dimethylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, o-ethylphenol, m-ethylphenol, p-ethylphenol, p-propylphenol,
15 p-butylphenol, 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol or α -naphthol. Of these, we particularly prefer those phenols having no substituent at the ortho position.

Examples of aromatic carboxylate esters (ii), which may be used to prepare the solid carrier used in the composition
20 of the invention, include methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, phenyl benzoate, methyl p-methoxybenzoate, ethyl p-methoxybenzoate, propyl p-methoxybenzoate, butyl p-methoxybenzoate, phenyl o-methoxybenzoate, methyl p-ethoxybenzoate, cyclohexyl p-ethoxybenzoate, methyl p-methylbenzoate,
25 butyl p-methylbenzoate, cyclohexyl p-methylbenzoate,

ethyl o-methylbenzoate, phenyl p-butylbenzoate, diethyl phthalate, di-2-ethylhexyl phthalate or dimethyl terephthalate. Of these, we prefer compounds of formula $R^6-C_6H_4-COOR^7$ (in which R^6 and R^7 , which may be the same or different, each represents a hydrocarbon group having from 1 to 10 carbon atoms and the group represented by R^6 may be at any position on the benzene ring). Examples of preferred compounds are methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, phenyl benzoate, methyl p-methylbenzoate, butyl p-methylbenzoate, cyclohexyl p-methylbenzoate, ethyl o-methylbenzoate and phenyl p-butylbenzoate.

Examples of titanium compounds and vanadium compounds which may be supported on the solid carrier prepared by reacting components (i), (ii) and (iii) include those titanium compounds represented by the general formula $Ti(OR^3)_mX_{(4-m)}$ (in which R^3 represents a hydrocarbon group having from 1 to 20 carbon atoms, X represents a halogen atom and m is a number such that $0 < m < 4$), vanadium tetrachloride and vanadium oxytrichloride. Examples of titanium compounds having the aforementioned formula include titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetraethoxytitanium, tetrapropoxytitanium, tetra-isopropoxytitanium, tetrabutoxytitanium, tetrakis(2-ethylhexyl) titanate, tetrastearyl titanate, ethoxytitanium trichloride, diethoxytitanium dichloride, triethoxytitanium chloride,

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phenoxytitanium trichloride, diphenoxytitanium dichloride, triisopropoxytitanium chloride, butoxytitanium trichloride, dibutoxytitanium dichloride, tributoxytitanium chloride, ethoxytitanium tribromide, diethoxytitanium dibromide, triethoxytitanium bromide, propoxytitanium tribromide, dibutoxytitanium dibromide and tributoxytitanium bromide. A single one of these compounds or a mixture of any two or more thereof may be used.

The synthesis of the solid composition of the invention is preferably carried out throughout under an inert atmosphere, for example of nitrogen or argon.

The reaction between the organomagnesium compound and the aryloxyaluminium compound is preferably effected in a solvent, preferably at a temperature of from -30°C to $+200^{\circ}\text{C}$, more preferably from -10°C to $+150^{\circ}\text{C}$. This reaction may be carried out by adding the aryloxyaluminium compound (as such or as a solution or suspension in a suitable liquid) dropwise to a solution of an organomagnesium compound, or vice versa. The time allowed for the reaction should be sufficiently long for the reaction to go to completion and this is usually 10 minutes or more, more preferably from 30 minutes to 5 hours. The molar ratio of organomagnesium compound to aryloxyaluminium compound is preferably from 1:10 to 10:1, more preferably from 1:2 to 5:1. Examples of solvents which may be used for this reaction include: aliphatic hydrocarbons, such as pentane, hexane, heptane and

octane; aromatic hydrocarbons, such as benzene, toluene and xylene; alicyclic hydrocarbons, such as cyclohexane and cyclopentane; and ethers, which may be represented by the general formula R^4-O-R^5 (in which R^4 and R^5 are the same or different and each represents a hydrocarbon group having from 1 to 20 carbon atoms or R^4 and R^5 , together with the oxygen atom to which they are attached, form a ring). Examples of such ethers include diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, di-sec-butyl ether, dipentyl ether, diisopentyl ether, dihexyl ether, dioctyl ether, diphenyl ether, dibenzyl ether, anisole, phenetole, methyl benzyl ether, tetrahydropyran and tetrahydrofuran. A single one of these solvents or a mixture of any two or more thereof may be used.

The solid reaction product is then separated from the reaction mixture and used in the reaction with the phenol (i) and the aromatic carboxylate ester (ii). In actual practice, the solid product (iii) is normally separated by filtration and may then be used as such or after thorough washing with a purified inert hydrocarbon solvent and may be used with or without drying. A solid reaction product containing from 0.01 to 2% by weight of aluminium is particularly preferred.

The reaction of the solid reaction product (iii) thus obtained with the phenol (i) and the aromatic carboxylate ester (ii) is preferably carried out in a solvent, preferably at a temperature of from -30°C to $+200^{\circ}\text{C}$, more preferably from

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-10°C to +150°C, to give the solid carrier for the catalyst. The reaction of these three reagents can be carried out either in a single step or in two steps, in which the solid reaction product is first reacted with the phenol and then the resulting product is reacted with the aromatic carboxylate ester or in which the solid reaction product is first reacted with the aromatic carboxylate ester and then the resulting product is reacted with the phenol. The times allowed for the reactions should be sufficient for the reactions to go to completion, generally at least 10 minutes, preferably from 30 minutes to 2 hours. We prefer to employ from 10 to 200 mmoles, more preferably from 30 to 150 mmoles, of phenol and from 0.1 to 20 mmoles, more preferably from 1 to 5 mmoles, of aromatic carboxylate ester per 1 g of solid reaction product (iii). The solvents preferably used in this reaction include: aliphatic hydrocarbons, such as pentane, hexane, heptane and octane; aromatic hydrocarbons, such as benzene, toluene and xylene; and alicyclic hydrocarbons, such as cyclohexane and cyclopentane. After completion of the reaction, the solid reaction product is preferably collected by filtration and may then be employed directly as the carrier or may first be thoroughly washed with a purified inert hydrocarbon solvent and then used, either with or without subsequent drying. The solid product thus obtained is an addition product of the magnesium compound with the phenol and the aromatic carboxylate ester. We particularly prefer that the solid product should show the stretch vibration of the phenolic hydroxy group at 3200 - 3600 cm^{-1} in its infrared absorption spectrum.

To prepare the solid composition of the present invention, a titanium compound and/or a vanadium compound is then supported on the carrier produced by the reaction of components (i), (ii) and (iii), preferably by the immersion method, in which
5 the titanium and/or vanadium compound is contacted with the carrier either as such or in an inert solvent. Suitable inert solvents include: hydrocarbons, such as heptane, hexane, benzene and toluene; and hydrogenated hydrocarbons, such as 1,1- or 1,2- dichloroethane, chlorobenzene or o-dichlorobenzene. The temperature
10 of this contact reaction is preferably in the range from ambient temperature to 150°C. After sufficient of the titanium and/or vanadium compound has been supported, the resulting solid composition is separated, preferably by filtration, and then preferably washed thoroughly with a purified hydrocarbon diluent. The
15 washed product may be used as such or it may first be dried. It is desirable to adjust the amount of titanium and/or vanadium compound supported in the solid composition, so that the content of titanium and/or vanadium atoms in the composition is from 0.01 to 30% by weight, more preferably from 0.1 to 10% by weight.
20 The resulting solid catalyst component has a favourable particle size and a narrow particle size distribution and exhibits superior catalytic performance. This is component (a) of the catalyst system employed in the polymerization process of the invention.

The organoaluminium compound used as component (b) of
25 the catalyst system is preferably a trialkylaluminium (such

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as triethylaluminium, tripropylaluminium, tributylaluminium or trihexylaluminium), a dialkylaluminium halide (such as diethylaluminium chloride, dipropylaluminium chloride, dibutylaluminium chloride or dihexylaluminium chloride), an alkylaluminium dihalide (such as ethylaluminium dichloride, propylaluminium dichloride, butylaluminium dichloride or hexylaluminium dichloride), an alkylaluminium sesquihalide (such as ethylaluminium sesquichloride, propylaluminium sesquichloride, butylaluminium sesquichloride or hexylaluminium sesquichloride) or an alkylaluminium alkoxide (such as dimethylaluminium methoxide, diethylaluminium ethoxide, diethylaluminium butoxide or dibutylaluminium ethoxide). A single one of these organoaluminium compounds or a mixture of two or more thereof may be used.

When polymerizing an α -olefin having 3 or more carbon atoms using the catalyst system of the present invention, it is desirable to use an electron-donating compound as a third component of the catalyst system, in order to improve the stereoregularity of the resulting polymer. Examples of such electron-donating compounds are amines, amides, esters, ethers, ketones, nitriles, phosphites, phosphines and sulphides, as are well known in the art. Of these, carboxylate esters, particularly aromatic carboxylate esters [such as those serving as component (ii) in the preparation of the solid reaction product] are particularly preferred. The amount of electron-donating compound

used is preferably from 0.01 to 1 mole, more preferably from 0.1 to 0.6 mole per mole of organoaluminium compound (b).

Examples of compounds which may be polymerized by the process of the invention include those ethylenically unsaturated compounds having from 2 to 15 carbon atoms, for example ethylene, propylene, butene-1, butadiene, 4-methylpentene-1, hexene-1, vinylcyclohexane, styrene and divinylbenzene. The polymerization can be carried out by the known slurry, gas phase or solvent methods, which are commonly used. It is desirable to employ a polymerization temperature of from ambient temperature to 200°C and a pressure from atmospheric pressure to about 100 atmospheres (about 101 bars), although the polymerization will proceed at higher temperatures and pressures. A molecular weight regulator, for example hydrogen, can be used. The polymerization may be carried out either continuously or batchwise.

Where a solvent is used as the polymerization medium, this is preferably an inert solvent, such as: an aliphatic hydrocarbon, such as propane, butane, pentane, hexane, heptane or octane; an alicyclic hydrocarbon, such as cyclohexane or cycloheptane; or an aromatic hydrocarbon, such as benzene, toluene or xylene. A single one of these solvents or a mixture of two or more thereof may be used. It is also possible to use a spent B-B fraction as the polymerization medium.

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The invention is further illustrated by the following Examples.

EXAMPLE 1

(a) Synthesis of magnesium compound

5 Into a flask flushed with argon were placed 25.8 g of
aluminium tri-o-cresoxide and 200 ml of dibutyl ether. The
resulting solution was heated to 50°C, and then there were
added dropwise, with stirring, 200 ml of a dibutyl ether solution
10 containing 0.247 mole of butylmagnesium chloride, over a period
of 1.75 hours. After completion of the addition, the mixture
was reacted for a further 2 hours at 50°C. The mixture was
then cooled to room temperature and filtered through a glass
filter. The white powder which collected on the filter was
15 washed twice, each time with 200 ml of heptane, and then dried
in vacuo, to give 28.2 g of a very flowable powder. The powder
contained 14.6%, 8.3% and 0.2% by weight of chlorine, magnesium
and aluminium, respectively.

(b) Synthesis of solid catalyst component

20 50 ml of a toluene solution containing 90 mmoles of
phenol and 6.3 mmoles of ethyl benzoate were added to 5 g of

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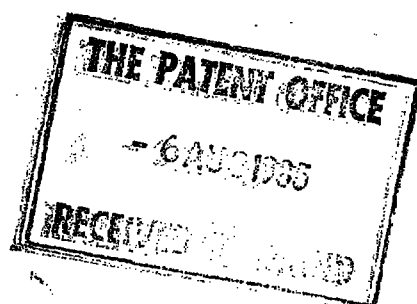
the magnesium compound obtained in step (a) above. The mixture was allowed to react at 60°C for 1 hour, after which the reaction product was collected by filtration and dried in vacuo. A portion of the resulting product was examined by infrared absorption spectroscopy (using thoroughly dehydrated Nujol-trade mark-mull). An absorption due to the phenolic hydroxy group was observed at 3 400 cm^{-1} and another absorption due to the carbonyl group of ethyl benzoate was observed at 1 680 cm^{-1} , indicating that the reaction product was a magnesium compound to which phenol or o-cresol and ethyl benzoate had been chemically added.

To the resulting reaction product were added 25 ml of titanium tetrachloride. The mixture was allowed to react for 2 hours at 100°C, after which the reaction product was thoroughly washed with heptane until no more titanium tetrachloride could be detected in the washings. The resulting solid catalyst component was then dried. On analysis, its titanium content was found to be 3.6% by weight.

(c) Polymerization of propylene

Into a 100 litre stainless steel autoclave which had been flushed with propylene were charged 100 mmoles of triethylaluminium, 100 mmoles of diethylaluminium chloride, 50 mmoles of ethyl p-anisate, 40 litres of hexane and 0.432 g of the solid catalyst component obtained in step (b) above. 27.5 litres

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(standard state) of hydrogen were charged into the autoclave and then propylene was fed into it and polymerization was continued for 4 hours at 70°C, whilst maintaining the gauge pressure at 8 kg/cm² by replenishing the propylene.

- 5 At the end of the predetermined polymerization time, polymerization was terminated by the addition of water and then the residual gas was purged. The polymer powder was separated from the hexane-soluble polymer. There were obtained 10.25 g of a dry polymer powder having an intrinsic
- 10 viscosity $[\eta]$ of 1.75 dl/g, (measured in tetralin at 135°C), a boiling heptane-extraction residue (II) of 97.7% and a bulk density of 0.42 g/ml. There were also obtained 179 g of a solvent-soluble polymer. The yield of polymer powder (HIP) was 98.3%. The polymerization activities
- 15 per gram of solid catalyst $[R(Y)]$ and per gram of titanium $[R(Ti)]$ were 24 100 g polypropylene per gram catalyst and 669 000 g polypropylene per gram titanium, respectively.

EXAMPLES 2 TO 12 AND COMPARATIVE

EXAMPLES 1 TO 3

- 20 (a) Preparation of solid catalyst component

A mixture of 5 g of the magnesium compound prepared as described in Example 1(a), a phenol and an aromatic carboxylate ester, of the types and the amounts shown in Table 1, were allowed to react in 50 ml of toluene at 100°C

25 for 1 hour. At the end of this time, the reaction product was then allowed _____

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to react with titanium tetrachloride, as described in Example 1(b). The reaction product was then thoroughly washed with purified heptane and dried in vacuo, to give a titanium-containing solid catalyst component having the titanium content shown in Table 1.

Table 1

Example No.	Phenol	
		mmole
2	Phenol	90
3	"	30
4	<u>p</u> -Cresol	"
5	<u>m</u> -Cresol	"
6	<u>o</u> -Cresol	"
7	2,4-Dimethylphenol	40
8	3,4-Dimethylphenol	"
9	α -Naphthol	"
10	Phenol	30
11	"	"
12	"	"
Comparative Example No.		
1	-	-
2	Phenol	30
3	-	-

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Table 1 (Contd.)

Aromatic ester		Ti wt%
	mmole	
Ethyl benzoate	6.0	3.0
"	4.2	2.7
"	"	2.9
"	"	3.2
"	"	2.5
"	3.5	3.0
"	"	3.1
"	"	3.3
Ethyl p-anisate	4.2	3.5
Ethyl p-toluate	"	3.3
Methyl p-toluate	"	3.0
-	-	3.8
-	-	5.0
Ethyl benzoate	4.2	3.9

(b) Polymerization of propylene

Into a 2.0 litre stainless steel autoclave which had been flushed with propylene were charged 4 mmoles of triethylaluminium, 4 mmoles of diethylaluminium chloride, 2 mmoles of ethyl p-anisate and 600 ml of thoroughly dehydrated and

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purified heptane, after which 35 - 40 mg of the solid catalyst component prepared as described above in step (a) were added. 148 ml (standard state) of hydrogen were charged into the autoclave and then the internal temperature of the autoclave was raised to 60°C and propylene was fed into it. Polymerization was continued at 70°C for 1 hour, whilst maintaining the internal gauge pressure of the autoclave at 6 kg/cm² by feeding in further propylene. After 1 hour of polymerization, the polymerization was terminated by adding 3 ml of ethanol, and unreacted propylene was purged. The polymer slurry was diluted with 600 ml of heptane heated at 60°C. The polymer powder was then separated by centrifugation and dried in vacuo at 50°C. The solution separated by centrifugation was concentrated to recover a solvent-soluble polymer. The results obtained are shown in Table 2.

Table 2

R(Y) g/g	R(Ti) g/g	HIP %	II%	Bulk density, g/ml
8750	292000	98.7	97.0	0.40
6610	245000	98.2	96.1	0.36
7050	243000	98.5	96.5	0.39
6800	213000	98.0	96.7	0.38
4620	185000	97.2	96.0	0.41
4590	153000	97.6	96.2	0.38
6750	218000	97.9	96.7	0.39
6530	198000	98.0	96.5	0.43
6910	197000	97.5	96.0	0.37
6500	197000	98.5	97.0	0.39
6450	215000	98.2	97.1	0.40
3380	88900	95.0	94.0	0.34
4700	94000	95.3	94.5	0.33
3520	90300	97.4	95.6	0.35

EXAMPLE 13

(a) Synthesis of magnesium compound

A magnesium compound, in the form of a white powder,

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was prepared by reaction of butylmagnesium chloride and aluminium tri-o-cresoxide, as described in Example 1(a), except that diethyl ether was used as solvent in place of the dibutyl ether and that the reaction temperature was the boiling point of the diethyl ether. The resulting powder was found to contain 15.3%, 7.2% and 0.4% by weight of chlorine, magnesium and aluminium, respectively.

(b) Synthesis of solid catalyst component

A mixture of 5 g of the magnesium compound prepared as described in step (a) above, 30 mmoles of phenol and 4.2 mmoles of ethyl benzoate was allowed to react in 50 ml of toluene at 100°C for 1 hour. The reaction product was then allowed to react with titanium tetrachloride, as described in Example 1(b), after which the reaction product was washed and dried, to give a solid catalyst component containing 3.0% by weight of titanium.

(c) Polymerization of propylene

Propylene was polymerized under the same conditions as described in Examples 2 to 12, but using the solid catalyst component prepared as described in step (b) above. The catalytic activity R(Y) was 6 990 g polypropylene per gram catalyst and

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R(Ti) was 233 000 grams polypropylene per gram titanium. The yield of polymer powder (HIP) was 98.1%.

COMPARATIVE EXAMPLE 4

A solid catalyst component containing 3.1% by weight
5 of titanium was prepared as described in Example 13(b), except
that the ethyl benzoate was omitted. Polymerization of propylene
was then carried out under the conditions described in Examples
2 to 12. The catalytic activity R(Y) was found to be 2 600 g
polypropylene per gram catalyst and R(Ti) was 83 900 g poly-
10 propylene per gram titanium. The yield of polymer powder (HIP)
was 95.0%.

EXAMPLE 14

Into a 2.0 litre stainless steel autoclave which had
been flushed with ethylene were charged 4 mmoles of triethyl-
15 aluminium, 32.0 mg of a solid catalyst component prepared as
described in Example 3 and 600 ml of heptane. Hydrogen was
charged into the autoclave to a partial pressure of 3.0 kg/cm^2
at 70°C , and then ethylene was polymerized at 70°C for 1 hour,
whilst maintaining the total pressure at 6 kg/cm^2 gauge by
20 the addition of further ethylene. At the end of the predetermined
polymerization time, polymerization was terminated by adding

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3 ml of ethanol, and the unreacted ethylene was purged. The polyethylene powder was collected by centrifugation and dried to give 346.12 g of a powder having the following properties: $[\eta] = 2.17$ dl/g; bulk density = 0.34 g/ml; a ratio of weight average molecular weight to number average molecular weight (M_w/M_n) = 10.7. The catalytic activity R(Y) was 10 800 g polyethylene per gram catalyst and R(Ti) was 400 000 g polyethylene per gram titanium.

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COMPARATIVE EXAMPLE 5

A titanium-containing solid catalyst component was synthesized as described in Example 3, except that the magnesium compound was replaced by o-cresoxymagnesium chloride (synthesized from butylmagnesium chloride and o-cresol in dibutyl ether). The resulting catalyst component contained 3.0% by weight of titanium. Using this solid catalyst component, ethylene was then polymerized under the conditions described in Example 14 to give a polyethylene having the following properties: $[\eta] = 2.40$ dl/g; bulk density = 0.32 g/ml. The catalytic activity R(Y) was 4 600 g polyethylene per gram catalyst and R(Ti) was 153 000 g polyethylene per gram titanium.

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EXAMPLE 15

(a) Synthesis of magnesium compound

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Into a flask flushed with argon were charged 13.9 g

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of aluminium tri-o-cresoxide and 60 ml of toluene. The resulting solution was heated to 100°C, after which there were added dropwise, with stirring, 58 ml of a dibutyl ether solution containing 0.13 mole of butylmagnesium chloride, over a period of 30 minutes. When the addition was complete, the mixture was allowed to react at 100°C for a further 2 hours. The reaction mixture was then cooled to room temperature and filtered through a glass filter. The white powder which was collected was then washed three times, each time with 100 ml of hexane.

10 (b) Synthesis of solid catalyst component

To the whole of the magnesium compound obtained as described in step (a) above were added 60 ml of a toluene solution containing 264 mmoles of phenol and 18.5 mmoles of ethyl benzoate. The mixture was allowed to react at 100°C for 1 hour. At the end of this time, the solid product was collected by filtration. To the solid product were added successively 150 ml of chlorobenzene and 70 ml of titanium tetrachloride. The mixture was then allowed to react at 100°C for 2 hours. At the end of this time, the solid product was washed repeatedly at 60 - 70°C with heptane until titanium tetrachloride could no longer be detected in the washings. The resulting solid catalyst component was dried and was found, on analysis, to contain 3.8% by weight of titanium.

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(c) Copolymerization of propylene and ethylene

Into a 100 litre stainless steel autoclave which had been flushed with propylene were charged 100 mmoles of triethylaluminium, 100 mmoles of diethylaluminium chloride, 50 mmoles of ethyl *p*-anisate, 40 litres of hexane and 0.512 g of the solid catalyst component prepared as described in step (b) above. 16.1 litres (standard state) of hydrogen were charged into the autoclave, after which propylene was polymerized for 4 hours at 70°C under a total pressure of 8 kg/cm² gauge, which was maintained by replenishing the propylene. The temperature was kept at 70°C, whilst the unreacted propylene was purged to a pressure of 0.1 kg/cm² gauge and hydrogen was charged to a pressure of 2 kg/cm² gauge, followed by ethylene to a pressure of 4 kg/cm² gauge. The ethylene was then polymerized for 1 hour and 40 minutes, whilst maintaining a total pressure of 4 kg/cm² gauge by replenishing the ethylene. The polymerization was then terminated by adding water and the residual gas was purged. The polymer powder was separated from the solvent-soluble polymer to give 11.51 kg of a polymer powder having the following properties: $[\eta] = 1.98$ dl/g; ethylene unit content = 36.5% by weight; bulk density = 0.42 g/ml. There were also obtained 226 g of a solvent-soluble powder. The yield of polymer powder (HIP) was 98.1%. The catalytic activity R(Y) was 22 900 g polymer per gram catalyst and R(Ti) was 603 000 g polymer per gram titanium. As can be seen from Table 3, the particle size

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distribution, as determined by vibrating sieves, was narrow, the fine particle content being low.

Table 3

Mesh of sieve	325	200	150	100	42	28	16	10
Cumulative % by weight of material passed through each sieve	0	0.18	0.61	1.5	8.2	22.5	80.1	99.5

The physical properties of the copolymer obtained were found to be as follows: Vicat softening point, 88°C; modulus of elasticity in flexure, 10 300 kg/cm²; gloss, 92%; haze, 67%; impact clouding, good. The tests were performed on a pressed sheet of 1 mm in thickness for Vicat softening point and modulus of elasticity and on an injection moulded sheet of 1.2 mm in thickness for gloss and haze.

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Claims

1. A solid composition comprising a titanium compound and/or a vanadium compound supported on a solid product formed from the reaction of (i) a phenol, (ii) an aromatic carboxylate ester and (iii) a solid reaction product of an organomagnesium compound and an aryloxyaluminium compound of general formula $Al(OR^1)_3$ (in which R^1 represents an aryl group having from 6 to 20 carbon atoms).
2. A composition according to Claim 1, in which said solid reaction product (iii) contains from 0.01 to 2% by weight of aluminium.
3. A composition according to Claim 1 or Claim 2, in which said solid product formed by reacting (i), (ii) and (iii) shows the stretch vibration of the phenolic hydroxy group at 3 200 to 3 600 cm^{-1} in its infrared absorption spectrum.
4. A composition according to any one of the preceding claims, in which said organomagnesium compound is a Grignard compound of formula R^2MgCl , in which R^2 represents a hydrocarbon group having from 1 to 20 carbon atoms.

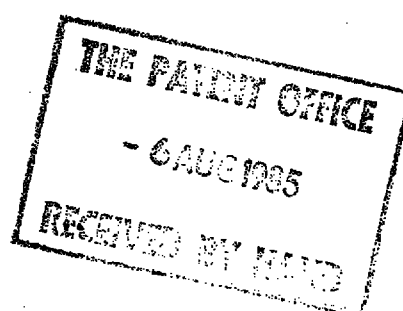


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5. A composition according to Claim 4, in which said Grignard compound is butylmagnesium chloride, ethylmagnesium chloride, pentylmagnesium chloride or octylmagnesium chloride.
6. A composition according to any one of the preceding
5 claims, in which said aryloxyaluminium compound is tricresoxyaluminium, triphenoxyaluminium or a mixture thereof.
7. A composition according to any one of the preceding
claims, in which said phenol (i) is phenol, m-cresol, p-cresol, 3,4-dimethylphenol, 3,5-dimethylphenol, m-ethylphenol, p-ethylphenol, p-propylphenol or p-butylphenol.
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8. A composition according to any one of the preceding
claims, in which said aromatic carboxylate ester (ii) is methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, phenyl benzoate, methyl p-methylbenzoate, butyl p-methylbenzoate,
15 cyclohexyl p-methylbenzoate, ethyl o-methylbenzoate or phenyl p-butylbenzoate.
9. A composition according to any one of the preceding
claims, in which said titanium compound is a tetravalent titanium compound.
- 20 10. A composition according to Claim 9, in which said titanium compound is titanium tetrachloride.

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11. A composition according to any one of Claims 1 to 8, in which said vanadium compound is vanadium tetrachloride or vanadium oxytrichloride.

12. A composition according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.

13. A process for preparing a polymer by polymerizing an ethylenecally unsaturated compound in the presence of a catalyst system comprising:

(a) a solid composition according to any one of the preceding claims; and

(b) an organoaluminium compound.

14. A process according to Claim 13, in which said organo-aluminium compound is triethylaluminium, diethylaluminium chloride, trimethylaluminium, tributylaluminium, dibutylaluminium chloride or a mixture of any two or more thereof.

15. A process according to Claim 13 or Claim 14, in which said ethylenically unsaturated compound is ethylene, propylene, butene-1, 4-methylpentene-1, hexene-1 or vinylcyclohexane.

16. A process according to any one of Claims 13 to 15, in which the polymerization is carried out at a temperature of



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from ambient temperature to 200°C and at a pressure of from atmospheric pressure to 100 atmospheres (101 bars).

5 17. A process according to any one of Claims 13 to 16, in which the polymerization is carried out in the additional presence of an electron-donating compound.

18. A process according to Claim 17, in which said electron-donating compound is an aromatic carboxylate ester.

10 19. A process according to Claim 13, substantially as hereinbefore described with reference to any one of the foregoing Examples.

20. A polymer when produced by a process according to any one of Claims 13 to 19.

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